

A High-Field Emission Ionization Detector for Gas Chromatography

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In addition to the various ways, reviewed by Lovelock¹, of providing primary electrons for ionization in gases, high field emission may be used. The detector tube constructed by Haahti and Nikkari^{2,3}, which obviously depends on field emission, is reported to function only at high temperatures⁴. A field emission-type ionization detector working at normal pressure and temperature with argon as carrier gas is described in this communication.

At normal temperature and pressure the current in commercial argon between electrodes 1 cm apart and at a potential difference of 1 000 V is about 10^{-12} to 10^{-11} A. This current is considerably higher than that between clean electrode surfaces in purified argon. This is explained by the fact that oxide or tarnish films on the electrode surfaces and impurities in the gas may greatly enhance the electron emission due to high fields⁵.

If the voltage gradient is sufficiently high, there will be a small concentration of metastable argon atoms in the interelectrode space. At a certain concentration of vapour molecules with an ionization energy ≤ 11.6 eV, the probability of a collision leading to ionization between a vapour molecule and a metastable argon atom will be high. Because the rate of such a double impact ionization process is proportional to the square of the current⁶, an electron avalanche will result, where collisions between vapour molecules and metastable argon atoms occur as intermediate stages. With such a mechanism it should be possible to make the ionization current dependent on the concentration of vapour molecules in the electric field⁴.

On attempts to use the tube of Haahti

and Nikkari at lower temperatures the tube was observed to work according to an "all-or-none" principle; the current impulse started by a minimum vapour concentration was limited by the associated circuit only. Because the too rapid current rise could be due to secondary processes at the cathode (liberation of secondary electrons due to positive ions, photons, or metastables), different geometries and cathode materials were tested.

The experiments were made with commercial argon led into the ionization tube under test through a short chromatographic column. The gas rates varied between 50 and 200 cm³/min. The temperature was +18°C. The resistance in series with the ionization tube and the source of high voltage (800–1 200 V) was $6 \times 10^9 \Omega$. The potential difference across part of the series resistance was fed through a simple impedance converter into a potentiometric recorder.

With aluminium electrodes an increase of the interelectrode distance by $\sim 100\%$ and/or a decrease of the surface-area of the cathode to $\sim 1/20$ of the dimensions reported by Haahti and Nikkari³ led to a response roughly dependent on the concentration of organic vapour in the argon. The tube was observed to have a time lag of some seconds. With the aluminum electrodes a "dead period" was also observed; when the signal had passed, the sensitivity of the tube to the following samples of organic vapour was nil or greatly reduced during a time varying between 30 sec and several minutes. This "dead period" is suggested to be due to a transitory change of the emissive properties of the aluminum surface because of the local heating generated upon impact of positive ions. It is probable that when the tube constructed by Haahti and Nikkari is operated at an elevated temperature not only the concentration of metastables is higher because of the greater acceleration of electrons in the electric field, but also that tarnish films on the electrode surfaces are absent or differ structurally from those on the electrodes at low temperatures.

When the cathode was made of tungsten wire, a higher field was required to obtain the

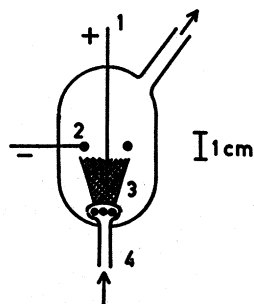


Fig. 1. Field emission ionization tube. 1. Platinum anode. 2. Tungsten cathode. 3. Diffusion net of 100 mesh metal gauze. 4. Gas inlet.

same sensitivity as with aluminum electrodes, but no "dead period" was observed. A platinum cathode behaved similarly, but a still higher field was required.

The smaller sensitivity but better correspondence to the concentration of dissociable vapour molecules in the carrier gas with the W and Pt cathodes could partly be due to the higher work function of these metals in comparison with aluminum. However, the work function of the cathode metal is considered to have little effect on the ionization of a gas at

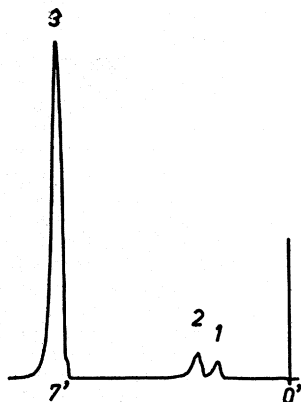


Fig. 2. Gas chromatogram obtained using the tube shown in Fig. 1 as detector. Anode-to cathode voltage: 1 000 V. Carrier gas: argon, 70 cm³/min. Column diam. 4 mm, length 20 cm, filling silicone M 550 on 40–60 mesh Firebrick. Column and detector temperature: +18°C. Outlet pressure 1 atm. 1. Ethyl ether. 2. Ethyl formate. 3. Cyclohexane. About 1 µg mixture injected.

atmospheric pressures because the surface has an adsorbed gas layer⁶. The view that gas or vapour layers sorbed on the cathode surface play an important role in the low-temperature field emission ionization detector is supported by the facts that (a) if the tungsten cathode has been heated to about 500°C by passing a current through it, the background ionization current in the tube is lowered and the sensitivity is nil until the cathode has been kept at room temperature in an argon stream for 1 or 2 h; (b) in nitrogen from a sample of organic vapours a signal current is obtained which over a wide range is independent of vapour concentration ($\sim 1:10^6$ to $\sim 1:10^8$). The signal current in this case is small, about 10 to 20 % of the background ionization current, because of the lack of gas amplification which occurs in argon through the production of metastables.

With all the cathode materials tested large oscillations of the signal current were frequently observed. This is thought to be due to disturbances caused by the gas stream of the space charge between the electrodes¹. A stable signal current was obtained by inserting a diffusion net of fine metal gauze. A workable electrode arrangement for a field emission ionization detector working with argon at room temperature, and a gas chromatogram obtained with this detector are shown in Figs. 1 and 2. The tube has been tested with, and found to respond to hydrocarbons, alcohols, aldehydes, ethers, and esters. Its relative response to different compounds varies considerably. The background current of the tube is 5×10^{-12} A, and the noise level is about 5 % of this.

A more detailed report will be published elsewhere.

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